Electron Interactions and Scaling Relations for Optical Excitations in Carbon Nanotubes

C.L. Kane, E.J. Mele

Dept. of Physics and Astronomy, University of Pennsylvania, Philadelphia, PA 19104

Recent fluorescence spectroscopy experiments on single wall carbon nanotubes reveal substantial deviations of observed absorption and emission energies from predictions of noninteracting models of the electronic structure. Nonetheless, the data for nearly armchair nanotubes obey a nonlinear scaling relation as a function the tube radius R. We show that these effects can be understood in a theory of large radius tubes, derived from the theory of two dimensional graphene where the coulomb interaction leads to a logarithmic correction to the electronic self energy and marginal Fermi liquid behavior. Interactions on length scales larger than the tube circumference lead to strong self energy and excitonic effects that compete and nearly cancel so that the observed optical transitions are dominated by the graphene self energy effects.

The optical transition energies of semiconducting nanotubes, along with their dependence on the nanotube diameter and chiral angle have been studied in a recent series of fluorescence spectroscopy experiments [1, 2, 3]. Though the experiments were originally interpreted in the context of a simple non interacting electron model, it has become increasingly clear that electron interactions play an important role in determining the optical transition energies[4, 5, 6, 7]. As pointed out in early work by Ando[4], interactions lead to (1) an increase in the single particle energy gap and (2) binding of electrons and holes into excitons. More recently, Spataru et al.[6] have reached a similar conclusion by computing the optical spectra for selected small radius nanotubes. However, the systematic dependence of the transition energies on nanotube radius has not been addressed.

In this paper we examine the optical excitations of carbon nanotubes in the limit of large radius, R, where they inherit their electronic structure from that of an ideal sheet of two dimensional (2D) graphene. This permits a systematic study of the radius and subband dependence of the excitations to leading order in $1/R$. In this limit the electron interactions fall into two categories: (1) 1D interactions on scales longer than the tube circumference, and (2) 2D interactions on scales smaller than the tube circumference. We find that the 1D long range interaction (1) leads to both a substantial enhancement of the energy gap and a large exciton binding energy which both scale as $1/R$. Although both effects are large they have opposite sign and ultimately lead to a moderate enhancement of the predicted optical transition energy. By contrast, we find the 2D interactions (2) lead to a $\log R/R$ correction to the bandgap renormalization. This singular behavior can be traced to the effect of a the Coulomb interaction on the dispersion of 2D graphene, which leads to marginal Fermi liquid behavior[8]. This logarithmic correction is not cancelled by the exciton binding energy, and leads to a nonlinear scaling dependence of the transition energies on R. The presently available optical data

indeed show this non linear scaling behavior and agrees favorably with the predictions of the large radius theory even for tubes with moderately small radii $R \sim 0.5$ nm.

Below we review the non interacting electron predictions for the energy gaps of semiconducting tubes and show that they can not explain the nonlinear scaling behavior present in the observed transition energies. We then present the theory for large radius tubes, focusing first on the effect of the 2D interaction on scales shorter than the circumference. We then incorporate the longer range 1D interactions into the theory.

The simplest model of nanotube electronic structure, based on non interacting electrons in a linear graphene spectrum, predicts that the energy gaps of semiconducting nanotubes are

$$E_n^0(R) = 2n\hbar v_F/3R, \qquad (1)$$

where R is the nanotube radius, $n = 1, 2, 4, 5$ describes the 1st, 2nd, 3rd and 4th subbands, and v_F is the graphene Fermi velocity. For a tight binding model on a honeycomb lattice with with lattice constant a and a nearest neighbor hopping amplitude γ_0, $\hbar v_F = \sqrt{3}\gamma_0 a/2$. The linearized model (1) is exact in the limit of large radius, and is the first term in an expansion in powers of $1/R$. Corrections due to curvature[9] and trigonal warping[10] are proportional to $\nu \sin 3\theta/R^2$, where θ is the chiral angle ($\theta = 0$ denotes an armchair wrapping) and $\nu = \pm 1$ is the chiral index. A central prediction of the non interacting model is thus that for large R the band gaps scale linearly with n/R - a fact that can be traced to the linear dispersion of graphene at low energies. The large R limit is most accurate for nearly armchair nanotubes for which the $\sin 3\theta$ corrections are smallest. For such tubes Eq. 1, describes the tight binding energy gaps to better than 1% for tubes with radii as small as 0.5 nm. The next term in the expansion at $\mathcal{O}(1/R^3)$ is negligible. Here we focus exclusively on nearly armchair nanotubes, where large R scaling can be meaningfully applied. $\sin 3\theta$ corrections, when present in
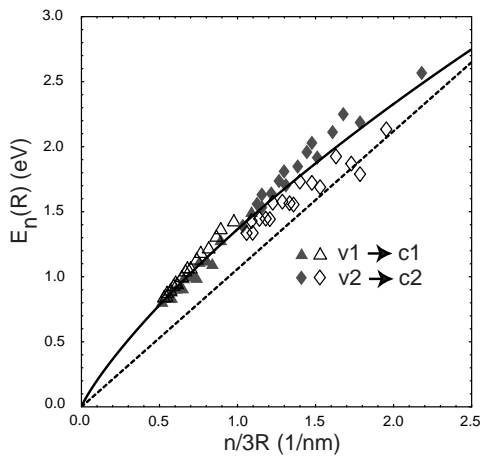
FIG. 1: Optical transition energies in the first two subbands for semiconducting nanotubes measured in Ref. 1 as a function of $n/3R$. The filled/open symbols correspond to $[p,q]$ nanotubes with chiral index $\nu = p - q$ mod $3 = +/-1$. The dashed line is prediction of the non interacting theory. The solid line is Eq. (4), which incorporates the effect of the 2D Coulomb interaction.

specific nanotubes, lead to deviations from the scaling predictions[6, 7].

The observed transition energies do not obey this linear scaling behavior. Extrapolated to large radius, the ratio between the first two transition energies appears to saturate at a value of 1.7, rather than 2 - a fact we have called the "ratio problem" [5]. In addition, the observed transition energies are systematically larger than the non interacting prediction. A nearly armchair nanotube of radius 0.5 nm has an observed first subband gap of 0.98 eV, which corresponds to Fermi velocity of 7.35 eVÅ. This value is significantly larger than the value 5.3 eVÅ found in graphite and the value 6.1 eVÅ deduced from resonance Raman data. The "blue shift" cannot be represented by a simple scaling of the transition energies since it is larger for larger radius tubes and therefore not linearly proportional to n/R.

In Fig. 1 we plot the transition energies reported in Ref. 1 as a function of $n/3R$, where n is the subband index, and R is the tube radius deduced in Ref. 1 by exploiting the pattern of $\sin 3\theta/R^2$ corrections. We have used different symbols to represent the data with $\nu = \pm 1$. The separatrix between the data for the positive and negative ν locates the data for the nearly armchair tubes with $\theta \sim 0$. At the separatrix the $\sin 3\theta/R^2$ corrections are absent, so that the radius dependence should be described by the large R limit to order $\mathcal{O}(1/R^3)$. It is clear, however, that even at the separatrix, the linear scaling relation (1) is not satisfied. Nonetheless, it is striking that the data near the separatrix for the two subbands lie approximately on the same nonlinear curve. The simplest interpretation of this apparent scaling behavior is

that these energies probe the dispersion of 2D graphene at a wavevector $q_n = n/3R$. This suggests that the ratio problem and the blue shift problem have the same origin.

Gonzalez et al.[8] have shown that the Coulomb interaction in 2D graphene leads to a singular correction to the electron self energy. Consider the Hamiltonian

$$\mathcal{H} = \hbar v_F \int d^2 r \psi^\dagger \vec{\sigma} \cdot \frac{\vec{\nabla}}{i} \psi + \frac{e^2}{2} \int d^2 r d^2 r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (2)$$

where ψ is a Dirac spinor with two copies for the K-K' degeneracy, and $n = \psi^\dagger \psi$. The Coulomb interaction is characterized by a dimensionless interaction strength $g = e^2/\hbar v_F$. In lowest order perturbation theory the electronic dispersion is

$$E(q) = \hbar v_F q[1 + (g/4) \log(\Lambda/q)], \quad (3)$$

where Λ is an ultraviolet cut off of order the inverse lattice constant. The nonlinear behavior as $q \to 0$ is a consequence of the long range singularity of the 2D Coulomb interaction $V(q) = 2\pi e^2/q$. It is thus important to account for screening. The semi-metallic Dirac spectrum of graphene leads to a static polarizatibility $\Pi(q) = (1/4)q/v_F$. The linear dependence on q exactly cancels the $1/q$ singularity of $V(q)$, leading to a multiplicative renormalization of the interaction analogous to screening in a 3D dielectric. The $q \to 0$ logarithmic correction to $E(q)$ survives screening although its coefficient is renormalized. In a static screening approximation the renormalized interaction is $g_{\mathrm{scr}} = g/(1 + g\pi/2)$.

Though it is derived in for small g, this result has deeper implications, since it shows that the weak interaction limit is perturbatively stable. (3) is invariant under the renormalization group (RG) transformation $\Lambda \to \Lambda e^{-\ell}$, $g \to g(\ell)$, $v_F \to v_F(\ell)$ with

$$dg/d\ell = -g^2/4; \qquad dv_F/d\ell = v_F g/4. \quad (4)$$

We may interpret (3) in terms of a scale dependent renormalization of v_F and g. The interaction vertex $e^2 = \hbar v_F g$ is not renormalized, so that the scaling is characterized by a single parameter g. Eq. (4) shows that g is marginally irrelevant: at long wavelengths g becomes smaller and perturbation theory becomes better. This implies that even for strong interactions the system flows to the perturbative limit at long wavelengths where (3) and (4) are valid. Therefore, the dispersion for small q is given exactly by (4) with renormalized parameters v_F and g, which depend on the cutoff scale Λ. We thus have a situation similar to Fermi liquid theory, where low energy quasiparticles behave like non interacting particles, albeit with renormalized parameters. Here, however, the marginal irrelevance of g leads to logarithmic corrections which do not disappear at low energies. As emphasized by Gonzalez et al.[8], this singular behavior is a signature of a marginal Fermi liquid.

Though (3) is exact for $q \to 0$, it remains to determine the values of the renormalized parameters v_F and g when the bare interactions are strong. Using the Fermi velocity of bulk graphite (where 3D screening eliminates the logarithmic singularity), $\hbar v_F^0 = 5.3$ eVÅ we estimate a bare interaction strength of $g_0 = e^2/\hbar v_F^0 = 2.7$ at a cut off scale Λ_0 of order the inverse lattice constant. A crude estimate of the renormalized parameters may then be obtained by extrapolating (4) to strong coupling using $g = (g_0^{-1} + (1/4) \log \Lambda_0/\Lambda)^{-1}$. For $\Lambda \sim .5\text{nm}^{-1}$ this gives $g \sim 1.1$ and $\hbar v_F \sim 12.9$ eVÅ. A more accurate theory requires knowledge of the form of the RG flow equations (4) for strong coupling and requires an approximation. Gonzalez et al.[8] have developed a GW approximation, which incorporates a dynamically screened Coulomb interaction. A simpler theory can be developed within a statically screened approximation. We find that the results agree within 5% with the dynamically screened theory[11]. For static screening the renormalized dispersion has the same form as (3) with g replaced by $g_{\text{scr}} = g/(1 + g\pi/2)$. The RG flow equations are similarly modified with a factor of $(1 + g\pi/2)^{-1}$ on the right hand side of (4). This leads to a refined estimate of the parameters at $\Lambda \sim .5\text{nm}^{-1}$: $g = 2.0$; $\hbar v_F = 7.2$ eVÅ. The screened interaction is $g_{\text{scr}} = 0.48$.

The nonlinear scaling form of the separatrix in Fig. 1 is consistent with Eq. (3). Choosing the scale $\Lambda = 0.5\text{nm}^{-1}$, the data is well fit with the parameters $v_F = 7.8$ eVÅ and $g = 0.74$. These parameters are in acceptable agreement with the statically screened theory described above, given the theory's simplicity. The 2D interactions in graphene appear to explain the nonlinear scaling of the data in Fig. 1 and thus resolve both the ratio problem and the blue shift problem.

Nevertheless the agreement between the data and the interacting theory of 2D graphene is surprising because the latter does not account for excitonic effects, which are known to be large[4, 6, 7]. To describe excitons it is essential to account for the 1D interactions on scales *larger* than R. In addition to exciton binding, these interactions lead to an increase of the single particle energy gap. To address this issue we have numerically calculated both the single particle and particle-hole gaps. We find that the two 1D interaction effects largely cancel one another, so that the R dependence of the particle-hole gap is ultimately well described by the 2D theory. We will begin by discussing our numerical calculation. We then show how these conclusions can be understood within a simple 1D model.

We have computed the the single particle and particle hole energy gaps for nanotubes in a statically screened Hartree-Fock approximation. Our calculation is similar to that previously reported by Ando[4], though here we focus on the R dependence of the energy gaps. We use a π electron tight binding model, which includes all 1D subbands. To avoid the complications associated with the
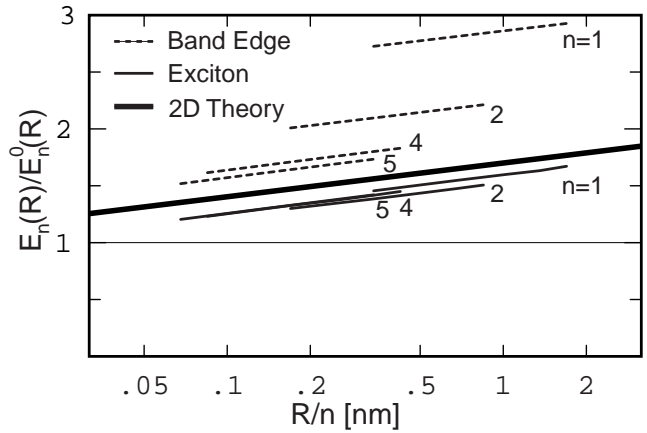
FIG. 2: Single particle gaps (dashed line) and particle hole gaps (solid line) for the first four subbands of semiconducting $[p,p]$ nanotubes with phase shifted boundary conditions calculated for $5 < p < 25$. The thick line is the prediction of the 2D theory Eq. 4.

$\nu \sin 3\theta/R^2$ corrections we study semiconducting tubes by calculating excitations of armchair tubes with an appropriate phase shifted boundary condition impose an energy gap. The single particle band gaps are computed by evaluating the exchange self energy using a statically screened Coulomb interaction. The particle-hole gap is determined by numerically diagonalizing the Schrodinger equation for the particle and the hole in the renormalized bands bound by the screened interaction. This is equivalent to solving the Bethe-Salpeter equation in the static screening approximation.

In Fig. 2 we plot the single particle and particle hole gaps as a function of radius and subband index. To emphasize the corrections to linear scaling behavior we provide a log-linear plot of $E_n(R)/E_n^0(R)$ as a function of R/n, where E_n^0 is given by (1), and is proportional to n/R. The prediction based on the statically screened 2D theory of graphene given in (4) is shown for comparison [12]. The single particle gaps are strongly enhanced relative to their non interacting values, while the particle-hole gaps are only moderately enhanced. Thus, most of the enhancement of the single particle band gap is cancelled by the electron hole interaction that binds the exciton. Moreover, since the slopes of all of the curves is the same in Fig. 2, both the single particle and the particle hole gaps exhibit the same logarithmic increase with radius. The excitonic binding energy, which is the difference between the two, does not have the logarithmic increase, and scales inversely with R. The particle-hole gaps for the different subbands lie nearly on a *single* straight line, close to the prediction of the 2D interacting theory. This is consistent with the scaling behavior in the experimental data in Fig. 1. In contrast, the single particle gaps are well above the predictions of the 2D theory, and do not obey scaling with subband index.